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Prevention of Formation of Flaws
During Crystallization of Steels,
With the Aid of Rare Earth Elements

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The possibility of sharp reduction or prevention of formation of non-axial irregularities (flaws) in ingots may be effected by addition to the deoxidized liquid steel of a mixture of rare earth elements, which will cause the separation of a sulphide phase at an earlier stage of crystallization.

The present article deals with the possibilities of influencing the irregularities in distribution of sulphur and other impurities during the crystallization process of steel by means of the addition of rare earth elements.

The following explanation can be assumed for the formation of flaws in ingots. The shrinkage cavities which are formed during crystallization in a two-phase zone are subsequently filled with the liquid solution flowing into said cavities; said solution being enriched by the impurities from the upper inter-axial dendritic spaces, resulting in formation of the flaws. When the crystallization is at a slow rate (in large ingots) the flaws will be in the form of elongated streaks.

The diffusion of the impurities will be substantially accelerated due to the contraction movement of the liquid in the two-phase zone, thus sharply increasing the flaws. The generation of gases may increase the movement of the liquid and thus of the development of the non-axial irregularity, but the flaws will form regardless of the generation of gases.

By an appropriate action on the liquid steel, it is possible to induce a separation of sulphur from the solution in the form of a dispersive sulphide phase in an earlier stage of crystallization; this would substantially lower the accumulation of the sulphides between the crystallites, thus substantially reducing the accumulation of the sulphides in the form of flaws.

The prevention of the accumulation of sulphur in the flaws will also reduce the accumulation of other impurities therein (carbon, phosphorous and others), because the accumulation of sulphur will reduce the temperature of solidification of the last portions of the liquid solution, thus increasing the accumulation of other dissolved impurities.

As a reagent for the physical-chemical treatment of the liquid steel, a mixture of rare earth elements, which primarily consists of cerium and lanthanum metal, is preferably used.

A. METHOD OF INVESTIGATION

For the purpose of investigating the influence of rare earth metal on the distribution of sulphur and other impurities in the crystallization of steel, comparative ingots were used with additions and without additions (control ingots) which were cast in sand molds, the cast being made from the same melt.

Cooling in sand molds permits the formation of relatively intensive flaws in a steel of conventional composition in ingots of small dimensions.

For the investigation purposes, three types of ingots were cast (compare Table No. 1). The test ingot (No. 4) weighed about 450 kgr. (990 lbs.) but the following ingots (Nos. 6, 7 and 8) were lighter and reduced to approximately 300 kgr. (660 lbs.), which filled out the molds only to approximately 700 mm. (28 inches).

It was possible further to reduce the weight of the ingots down to approximately 200 kgr. (440 lbs.) with the diameter of the top and bottom of the ingot being 260 (10 inches) and 235 mm. (9-1/4 inches) respectively. Despite the reduced size, the control ingots made of the steel "40N", prone to form flaws, showed a sufficiently intensive development of the flaws.

The steel was melted in acid induction furnaces of a capacity of 1000 and 600 kgr. (2200 to 1320 lbs.). After reducing the steel with ferro-manganese or ferro-silicon, aluminum was added (1 lb./ton). The temperature of the liquid metal was measured by means of platinum rhodium - platinum thermo-couple immersed into the metal.

TABLE I — DETAILS OF TEST INGOTS

INGOT No.	DIMENSIONS (INCHES)			WT. LBS.	COMPOSITION — %*					
	DIAMETER		HEIGHT		C	Si	Mn	S	P	Ni
	TOP	BOTTOM								
4	11.42	10.63	33.5	990	0.36	0.32	0.59	0.045	0.037	—
6, 7, 8	11.42	10.63	27.5	660	0.39	0.23	0.66	0.024	0.025	1.15
9, 10, 11	10.24	9.25	19.7-21.6	440	0.42	0.39	0.37	0.035	0.025	1.10
12, 13, 14	10.24	9.25	19.7-21.6	440	0.41	0.30	0.37	0.032	0.024	1.12

*Ladle analysis

In the case where the additives were introduced into the steel in the molds, the steel was cast from ladles, and in all other cases the steel was placed in measured portions into the ladle, the capacity of which equals the weight of the ingots. The additives were introduced into the ladle at the pouring of the metal from the furnace. In all experiments except one, the melted steel was of the type "40N".

For the determination of the distribution of the additives were used not only the conventional methods of chemical and metallographic analysis but also the method utilizing radioactive atoms.

Radioactive isotopes in the form of elementary sulphur (S35) and red phosphorous (P32) were packed into hermetically closed steel ampules and were introduced into the furnace shortly before discharging the steel. The dosage was computed from the specific activity at the moment of exposure. For S35 the dosage was approximately 0.1 m. curie/kgr. and for P32 approximately 0.01 m. curie/kgr.

For the determination of the distribution of S35 and P32 in the ingots, radiograms were made from longitudinal and transverse plates or sections cut from the ingots; the exposure being 15 to 20 days. The method of radio photography was described previously (V. M. Tageev and V. A. Dudkin in "Proceedings of the Scientific-Technical Society of Ferrous Metallurgy", Vol. V Metallurgizdat 1955).

For a separate determination of the distribution of P32, a layer of heavy paper was disposed between the section and the roentgen film, serving as a filter for absorption of the radiation by S35. For simultaneous determination of P32 and S35 the film was placed directly on the section. Thereafter, for obtaining

simultaneously two such radiograms, two films were used, one film was utilized as a filter absorbing the radiation of S35. For a separate determination of the distribution of S35, radiograms were made approximately every 2.0 to 2.5 months (4 to 5 periods of half-decay periods of P32) after the start of the first exposure.

The simultaneous determination of the distribution of S35 and P32 on one film at their maximum specific activity (for instance, approximately 0.1 m.curie/kgr. S35 and approximately 0.005 m.curie/kgr. of P32) are of great interest, because the radiation of S35 gives sharply distinguishable spots, corresponding to the sulphide inclusions. The radiation of P32 gives a gradual change in the darkening of the radiogram corresponding to the continuous change in the concentration of phosphorous in the axes and in the intermediate spaces of the dendrites.

For the preparation of the sections, the ingots were first cut in lateral direction and subsequently in the longitudinal direction of the axes (thus consisting of a corresponding number of separate pieces.)

From the three melts were made two ingots each with additions of 0.05 to 0.2% of the Rare Earth Metal alloy, (No. 7 and 8; 10 and 11; 13 and 14) and one control ingot without any additives (No. 6, 9 and 12). Ingot No. 4 was cast from a fourth melt of carbon steel with the addition of rare earth elements.

The additives contained up to 43% of Ce and approximately 5% of Fe; the rest comprising lanthanum and other elements. The additives were introduced in the form of lumps placed at the bottom of the molds for the metal or in the ladles.

In all cases a radioactive isotope of phosphorous was added to the metal, and in casting the ingots No. 12, 13 and 14 a radioactive isotope of sulphur was added.

B. RESULTS OF THE INVESTIGATIONS

The chemical composition of the steel, and the basic characteristics of their structures in accordance with the results of the radiographic and metallographic methods are compiled in the Tables 1 and 2.

The carbon contents in the experimental melts was varied from 0.36 to 0.42%.

In all control ingots there could be observed a non-axial zonal irregularity - flaws in form of streaks (in the transverse section in the form of spots, and the longitudinal section - as strips).

In the photographs are shown negative images of the radiograms, therefore the light sections of the pictures correspond to increased concentration of the radio-active isotope in the metal, and consequently, of the corresponding isotope which is a conventional impurity in the metal. The darker section of the picture show the places of lower concentration of the isotope.

The addition of the liquid deoxidized steel of 0.05 to 0.10% of the rare earth metal alloy will substantially reduce the non-axial zonal irregularity of the ingots and casts. But the addition of 0.15 to 0.20% of said additive will practically prevent the formation of flaws.

In Fig. la is shown a section of a radiogram of a transverse section of the control ingot No. 6 obtained with the aid of P32. As can be seen, highly developed flaws are present, having in the transverse section the characteristic spots. The radiogram also shows the dendrite structure of the metal due to the enrichment of phosphorous in the intermediate spaces between the axes and the reduction of phosphorous along the axes.

In the radiograms of the transverse sections of ingots No. 7 and 8 (Figs. lb and lc), it can be seen that the addition of 0.1% of the alloy substantially reduces the formation of flaws, and that addition of 0.2% will prevent their formation.

In the longitudinal section of the control ingot No. 9 (Fig. 2) can also be seen an intensive formation of the flaws, which are particularly sharply contrasted at the side facing the cooling surface, and which are inclined to the vertical axis of the ingot.

When comparing the radiograms of the transverse sections, which were obtained with the aid of S35 and P32 by simultaneous introduction of same into the melt, a complete analogy of the distribution of sulphur and phosphorous in the steel or ordinary composition is seen (accumulation of same in the inter-axial spaces of the dendrites, in the flaws, etc.).

TABLE II — MACROSTRUCTURAL CHARACTERISTICS OF INGOTS

INGOT No.	Ce-La Addition		METAL TEMP. (°F)		Radiographic Examination**		Sulphur Prints	
	Lbs. T.	How Introduced*	Furnace	Tap	"Flaw" Formation	Other Irregularities	"Flaw" Formation	Other Irregularities
4	2	M	2860	—	Mild	Top accumulation rich in P	Practically None	Top-floating sulfides; uniform S distribution in ingot body
6	None	—	—	—	Strong	—	Strong	—
7	2	M	—	2820	Much lower than ingot #6 (Phos.)	As in ingot #4	None	Less "floating" sulfides than in #4; some sulfides in dendrite axes
8	4	M	—	2820	Practically None	As in ingot #4	None	Ratio of sulfides in dendrite axes greater than in #4
9	None	—	2930	—	Strong Phos. segregation	—	Strong sulfur segregation	—
10	1	L	2890	—	Weaker than ingot #9	—	Weaker than ingot #9	—
11	4	L	—	—	None	Structure coarser (?) than ingots #9 and 10	None	Part of sulfides in dendrite axes
12	None	—	2920	—	Strong accumulations (segregation) of S and P	—	Strong segregation of sulfides	—
13	3	L	2890	—	None	Substantial part of sulfides in dendrite axes; coarser (?) than #12	None	Substantial part of sulfides in dendrite axes
14	3	M	—	—	None	As in ingot #4; main portion of sulfides in dendrite axes	None	Top-floating sulfides; substantial part of sulfides in dendrite axes

*M=Mold addition; L=Ladle addition.

**Radioactive tracer isotope P32 used in all ingots; in addition, tracer S35 used in Ingots 12, 13, 14.

The radiograms as shown in Fig. 3 disclose that an addition of 0.15% (3 Lb./Ton) of a mixture of rare earth elements into the ladle (ingot of No. 13) also prevent the segregation of sulphur and phosphorous in the form of flaws.

The radiograms of the transverse sections of the ingots 9, 10 and 11 (Fig. 4) confirm that an addition into the ladle of 0.05 (1 Lb./Ton) of the rare earth alloy after discharge of a predetermined portion of the metal from the furnace slightly reduces the formation of the flaws, and that an addition of 0.2% (4 Lb./Ton) will prevent the formation of the flaws.

The results of the investigations of behavior of sulphur and phosphorous may be applied to any impurities, which have a different solubility in solid and liquid metal (particularly relative to carbon, tungsten, etc.) and also make possible certain conclusions with reference to the influence of the rare earth elements upon the characteristic distribution of sulphur and other impurities in the range of the crystallites.

When comparing the enlarged radiograms (Figs. 5 and 6), it can be determined that a part of the sulphide inclusions in steel to which rare earth elements were added is distributed in the axes of dendrites, and in steel without such additions in the inter-axial spaces.

Because these diagrams were obtained from the simultaneous radiation of S35 and P32, the axes of dendrites can be sharply seen in the range of which in steels with addition of the rare earth elements the sulphide inclusions can be easily found.

The analysis of this phenomenon permits the conclusion that an addition of rare earth elements to a deoxidized steel leads to separation of the sulphide phase in an earlier stage of crystallization, than in steel without rare earth additions. On the other hand, an earlier separation of the sulphide phase reduces the concentration of sulphur in the liquid solution in the inter-axial spaces of the dendrites.

Therefore, in case of steel with rare earth additions, the diffusive redistribution of sulphur is sharply reduced in the two-phase zone (molecular and convective diffusion), and therefore also the accumulation of sulphur in different forms of dendrite and zonal irregularity (trans and inner crystallite irregularities, flaws, etc.). Thus, the dendritic as well as zonal irregularities are reduced hereby.

Radiograms in Figs. 5 and 6 indicate that in steels with additions of rare earth elements the distribution of phosphorous in the range of crystallites (dendrite irregularity) is of conventional character, i.e., the accumulations can be observed in the inter-axial spaces and a reduced content of phosphorous along the axes of dendrites.

It therefore can be concluded that other impurities which are present in the solution during the crystallization will behave, in the range of the dendrites, in a manner similar to that of phosphorous. At the same time, the impurities which separate during the crystallization in the form of a dispersion phase, will distribute in the range of the dendrites in a manner similar to that of sulphur, when rare earth elements are added.

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Considering the diffusion contractive nature of the flaws, the above mentioned prevention of accumulation of other elements (except sulphur) can be explained in the following manner. The reduction of the concentration of sulphur in the liquid solution in the inter-axial spaces of the dendrites leads to an increase of temperature of solidification of the solution and a reduction of its mobility in the two-phase zone. Because of that, the movement of the liquid solution in the two-phase zone will be slowed down, and thus the accumulation of the dissolved impurities in the form of flaws will be weakened. Thus, by weakening of the dendrite irregularity, which is the source of the actual forms of zonal irregularity, the possibility of the formation and development of these forms is reduced. At the same time, when increasing the different forms of zonal irregularities (for instance of flaws) in connection with the local redistribution of the impurities, the dendrite irregularity of the adjacent sections will be reduced.

In casts made without addition of rare earth elements, under a thin skin of 2 to 3 mm. thickness can be observed larger separations of sulphide inclusions than in the skin itself, and a more irregular distribution of phosphorous. In the case of steel with rare earth additions, the structure of the skin layer is much more uniform, but the separation of the sulphide inclusions in the skin is larger. This confirms that the addition of rare earth elements will produce an earlier separation of the sulphide phase. Furthermore, when introducing into a liquid steel, at the bottom of the mold, a mixture of rare earth elements, sulphides, will be formed which will precipitate due to their lower solubility in liquid metal as a sulphide phase, float upwardly and will accumulate at the top portion of the ingot. A portion of the floating sulphide phase will be retained in the outer portions of the ingots due to the solidification of same, producing the characteristic flurry shaped accumulations.

In those cases where the rare earth elements were introduced into the ladle, this phenomenon could not be observed. Thus the addition of rare earth elements into the ladle is more favorable for production of more uniform ingots and melts, than the introduction of same into the molds.

Larger accumulations of sulphides in the upper portion of the crystallizing mass of the steel are indicated by the sulphur prints and diagrams obtained with the aid of S35 (Fig. 7a). Hereby the radiograms obtained with the aid of P32 will show that a higher concentration of phosphorous will also take place in the region of accumulation of the sulphides (Fig. 7b).

The results of the chemical analysis of the turnings from the sections of accumulation of the sulphides (Table No. 3, the drill having a diameter of 15 mm.) indicate that such a sulphide phase contains larger amounts of cerium, carbon and phosphorous than the metal in its cast stage.

This effect is produced due to the absorption of carbon and of phosphorous by the sulphide phase from the solution.

The accumulation of the sulphide phase floating upwardly (Fig. 7a) in its characteristic form does not have anything in common with the accumulation of sulphides

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in different forms of zonal irregularities (flaws, axial irregularities, accumulation of sulphides under the ingot pipe). In this way this phenomenon also contradicts the conception of formation of different forms of zonal irregularities as a result of the sulphide phase floating in the process of crystallization of steel.

In ingot No. 4 with the highest amount of floating sulphide phase, considering the initial content of sulphur of 0.045% and adding 0.1% of the rare earth alloy, the content of sulphur was reduced to 0.038%. But in ingot No. 8 - having a smaller quantity of the floating sulphide phase, and an initial content of sulphur of 0.024% and an addition of 0.2% of the rare earth alloy, a reduction of the sulphur content in the ingot could not be observed.

In the ingots No. 13 and 14 having initial content of sulphur of 0.032 and an addition of 0.15% of mixture of rare earth metals - a reduction of sulphur could not be observed (compare Table No. 3). This can be apparently explained by a relatively larger initial content of sulphur in the metal of ingot No. 4, than in the ingots 8, 13 and 14.

TABLE 111   Comparison of the Chemical Composition of the Metal in the Section of Accumulation of Floating Sulphides (BC), from the Body of the Ingot (TC), and During the Casting (P).

Ingot	Distance of point in mm from:		Chemical composition in %			
	Top (or bottom)	Surface	C	S	P	Ce.
4 BC	--	--	0.44	0.452	0.050	1.55
TC	140	15	0.38	0.038	0.033	0.03
P	--	--	0.36	0.045	0.037	--
8 BC	--	--	0.59	0.762	0.030	1.88
TC	200	15	0.39	0.023	0.025	traces
P	--	--	0.39	0.024	0.025	--
TC	(80)	15	--	0.033	--	--
13 TC	(80)	along axis	--	0.030	--	--
TC	100	15	--	0.033	--	traces
P	--	--	0.41	0.032	0.024	--
TC	(80)	15	--	0.033	--	--
14 TC	(80)	along axis	--	0.033	--	0.05
TC	100	15	--	0.033	--	.04
P	--	--	0.41	0.032	0.024	--

(7)

CONCLUSIONS

A possibility of reducing and preventing accumulations of sulphur and other impurities having different solubility in the solid and liquid phases, in forming flaws (not axial irregularity) in crystallization process of steel was determined. The improvement was obtained by treating the deoxidized liquid steel with additives, which will precipitate the sulphide phase at an earlier stage of crystallization. As such an additive, there can be preferably used a mixture of rare earth elements (cerium, lanthanum, etc.) in quantities of 0.10 to 0.20% (2 to 4 Lbs./Ton).

As a result of an earlier separation of the sulphide phase during the crystallization of steel under the influence of the rare earth elements, the diffusive redistribution of the sulphur in the two phase zone of the ingots (castings) will be substantially reduced. In this case a substantial portion of the sulphur will be distributed in the form of sulphide inclusions in the axes of dendrites, with corresponding reduction of the concentration of the same in the inter-axial spaces, and therefore reducing the dendrite irregularity of the steel (a more uniform distribution of sulphur in the range and on the edges of the crystallites).

This earlier separation of the sulphide phase will also reduce the irregularity of the structure of the skin layer (2 to 3 mm. thick).

At a substantially reduced dendrite irregularity the formation of accumulations of sulphur and other impurities in the form of flaws is prevented.

A more uniform distribution of phosphorous and other impurities is the result of reduced movement of the liquid phase in the two phase zone, apparently because of the reduced concentration of sulphur therein.

The determined effect of enrichening by phosphorous and carbon of the sulphide phase, which is formed and floats upwardly in the liquid steel, when treated with rare earth metals is of an absorbent nature.

The macrostructure of the investigated steel becomes slightly coarser as a result of addition of rare earth elements (0.05 to 0.20%).

The possibility of reducing by means of physical-chemical method the macroscopic irregularity of steel during crystallization was determined, and apparently can be rather advantageous also in the case of continuous casting in series production.
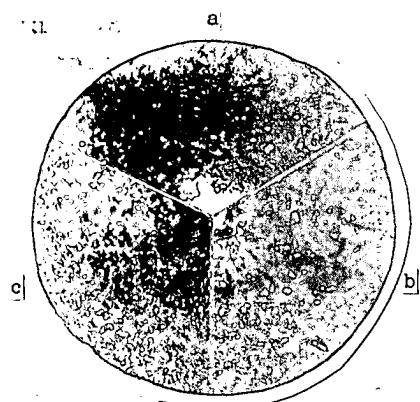
Fig. 1. Autoradiograms (P^{32}) of transverse sections of ingots from the same heat: a-Ingot #6 (control); b-Ingot #7 (0.1% alloy); c-Ingot #8 (0.2% alloy).

Fig 2. P^{32} autoradiogram of longitudinal section through Ingot #9 (control).
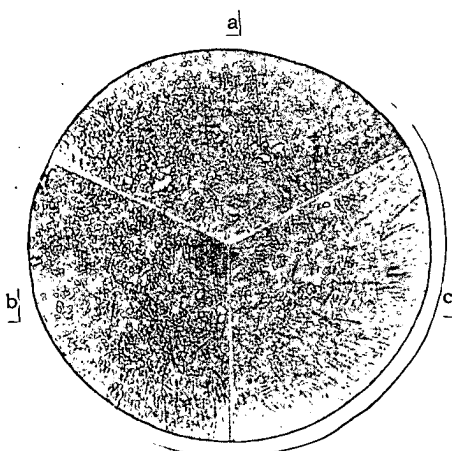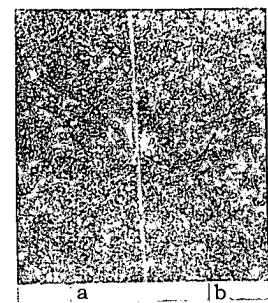

Fig. 3. S^{35} autoradiogram of transverse sections through ingots from the same heat: a- #12 (control); b - #13 (0.15% of the alloy added).

Fig. 4. P^{32} autoradiogram of transverse sections through ingots from the same heat: a- #9 (control); b- #10 (0.05% of the alloy added); c- #11 (0.2% of the alloy added).

Fig. 5. Four-fold enlarged radiogram (S^{35}, P^{32}) of zone of longitudinal section of ingot #12 (control); accumulations of S and P can be seen between the arms of the dendrites.

Fig. 6. Four-fold enlarged radiogram (S^{35}, P^{32}) of ingot #13 to which the alloy was added; part of the sulfide inclusions occur inside the dendrite arms.

Fig. 7. Radiogram of the upper part of a longitudinal plate from ingot #13 showing accumulations of floated-up sulfide phase: a- When using S^{35}; b- when using P^{32}.